Supporting Information

An autonomous device for solar hydrogen production from sea water

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Section S1. Anode preparation.

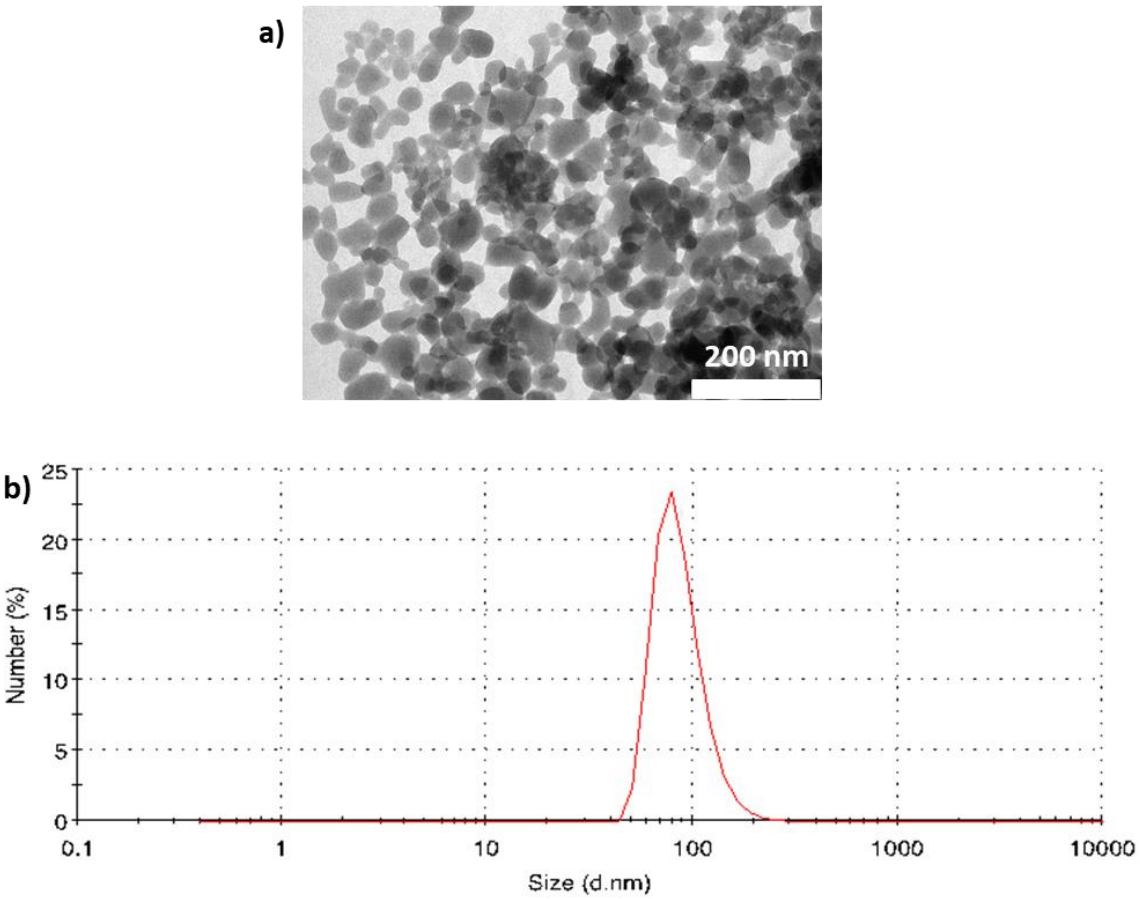


Figure S1. (a) TEM image and (b) Dynamic light scattering (DLS) obtained from CoFe-PB nanoparticles.

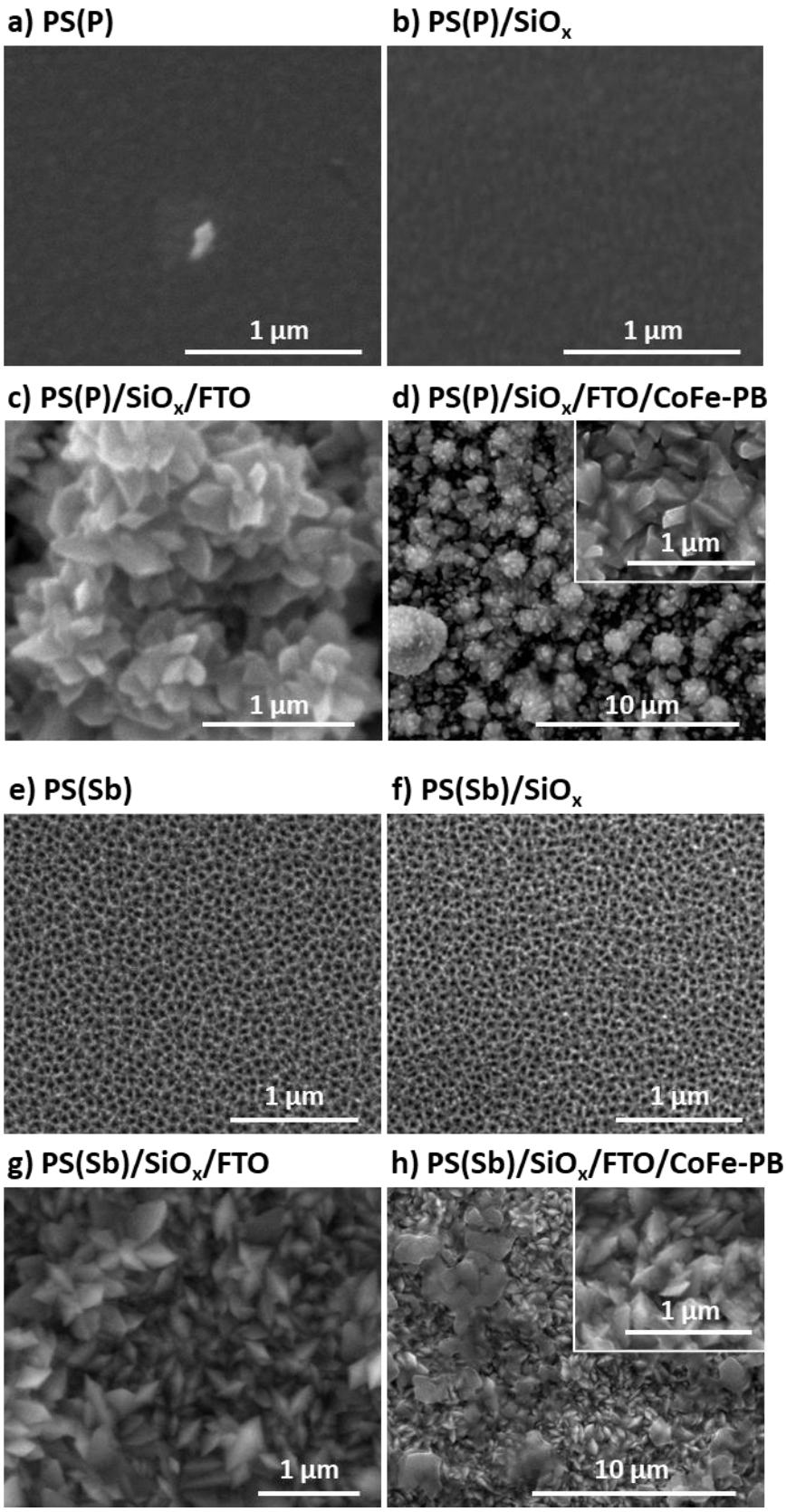


Figure S2. ESEM images obtained from (a-d) PS(P)/SiO_x/FTO/PB and (e-h) PS(Sb)/SiO_x/FTO/PB anodes after the different synthesis steps: (a,e) formation of porous silicon (PS) by anodization of n-type silicon wafers doped with P or Sb; (b,f) passivation of PS; (c,g) deposition of flurorine-doped tin oxide (FTO) by spray pyrolysis; and (d,h) deposition of cobalt iron prussian blue (CoFe-PB) nanoparticles by dip coating.

Section S2. Cathode preparation.

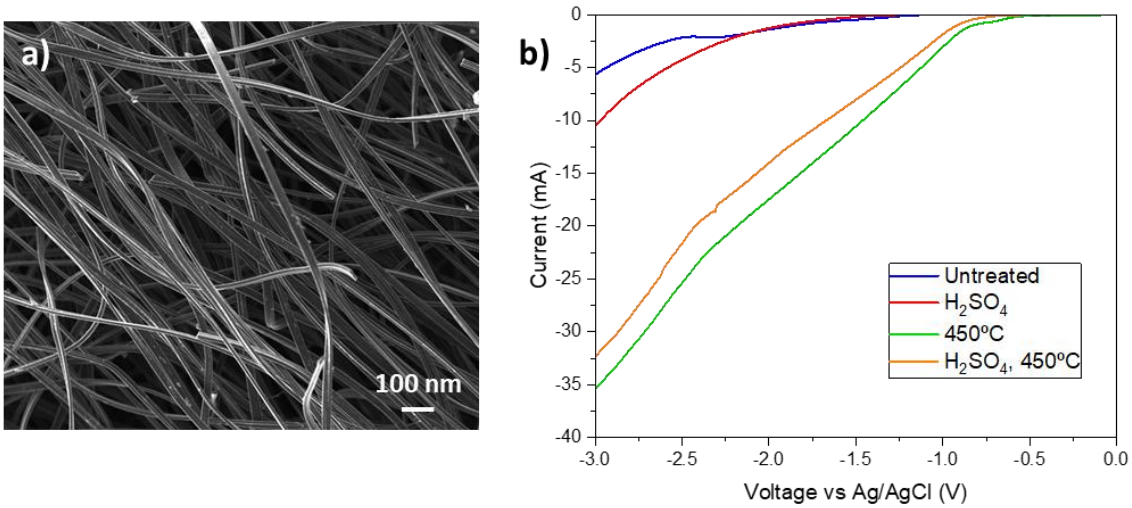


Figure S3. (a) ESEM image obtained from carbon felt cathode and (b) Linear sweep voltammetry of carbon felt cathode (used as working electrode) in seawater after different pretreatment conditions: i) untreated, ii) immersed in 1 M H_2SO_4 solution for 5 hours, iii) heated at 450ºC in air overnight and iv) combination of ii and iii. Pt mesh was used as anode (counter electrode).

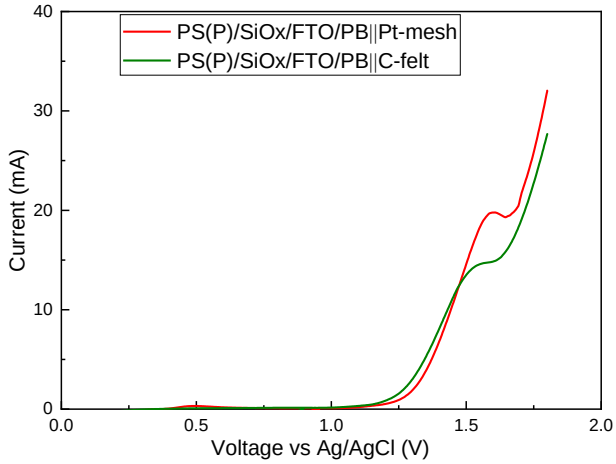
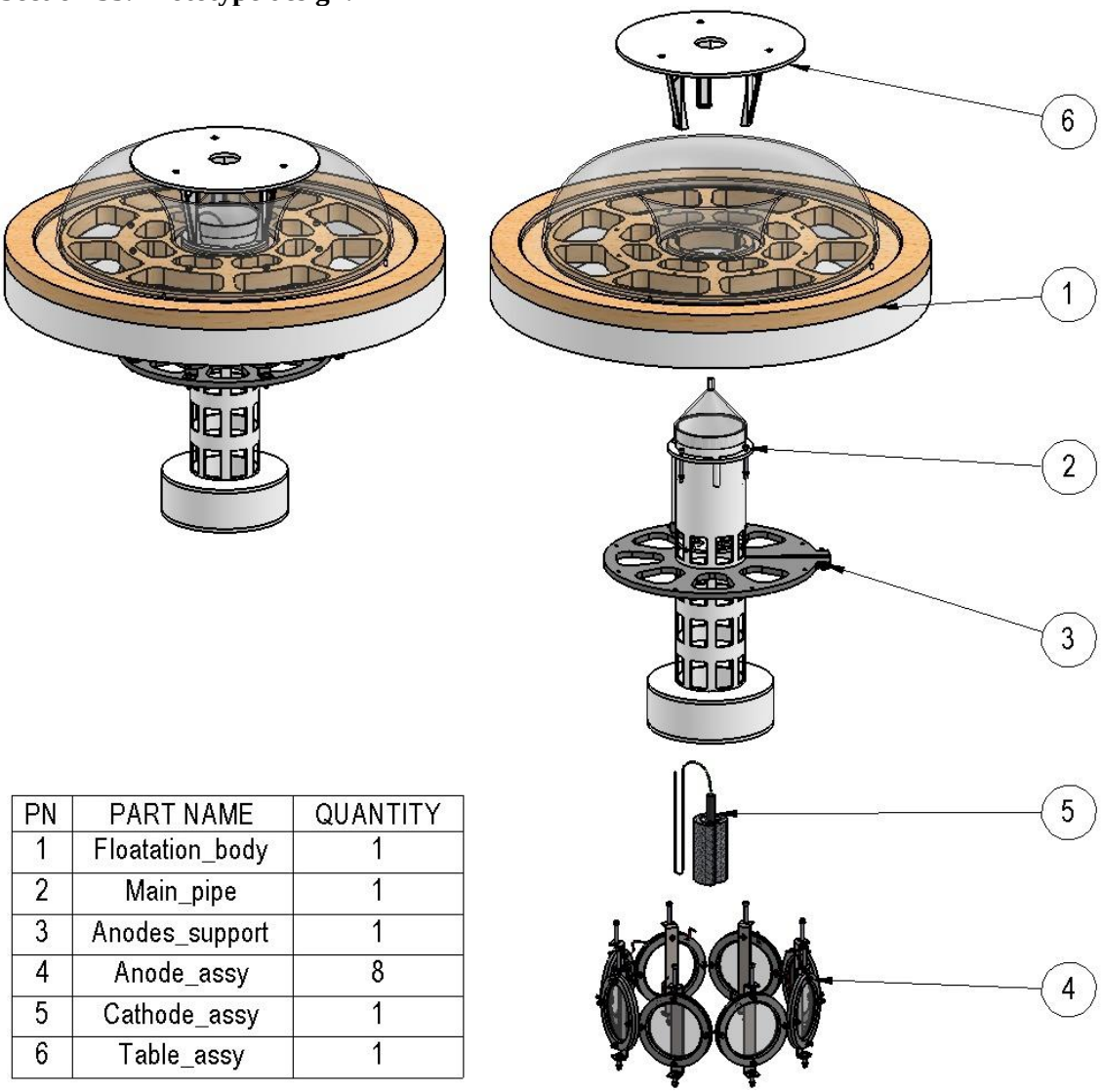


Figure S4. Linear sweep voltammetry of PS(P)/SiO_x/FTO/CoFe-PB anode in seawater using Pt mesh (1 cm x 1 cm) or carbon felt (1 cm x 1 cm x 1 cm) as cathode.

Section S3. Prototype design.

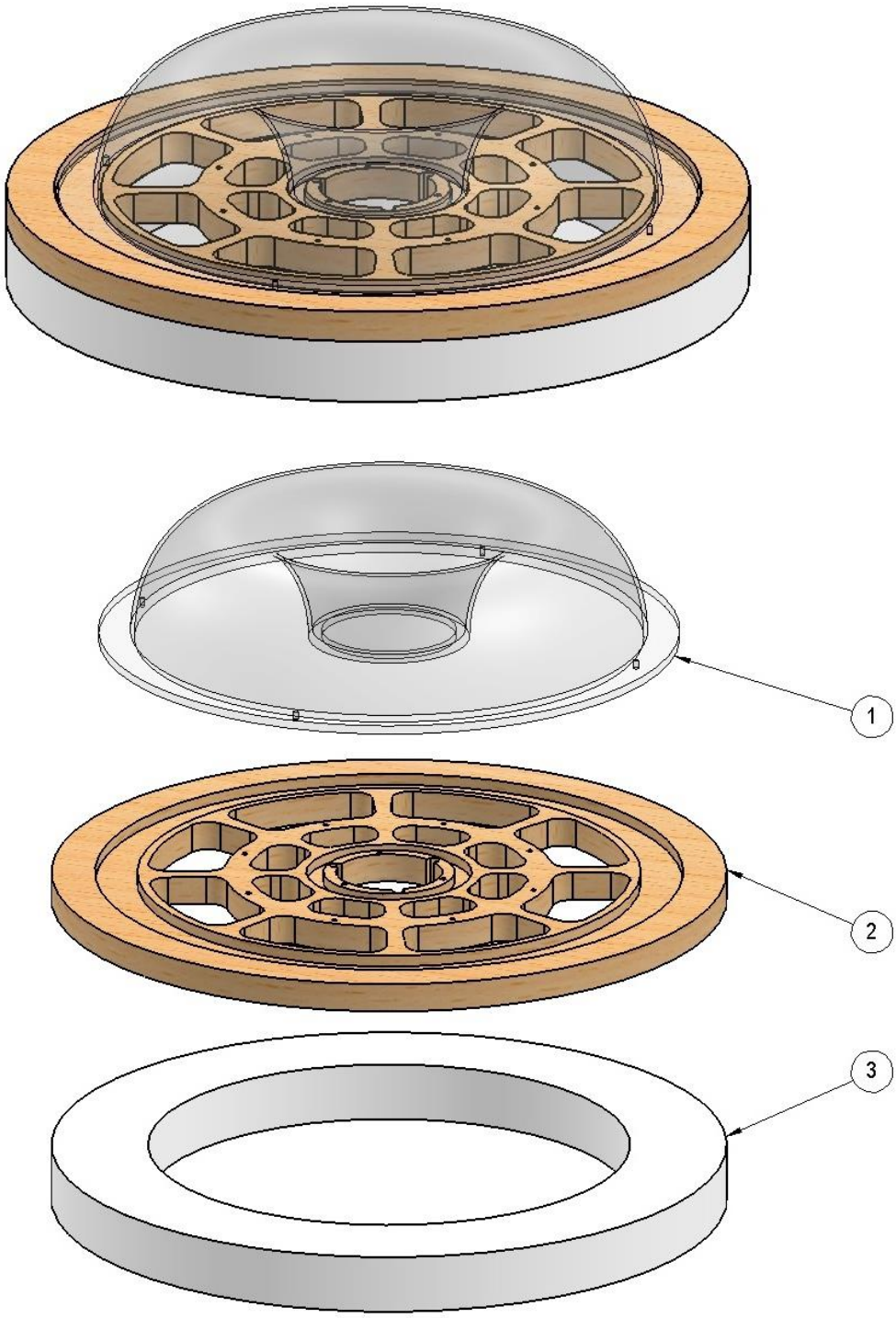


PN	PART NAME	QUANTITY
1	Floatation_body	1
2	Main_pipe	1
3	Anodes_support	1
4	Anode_assy	8
5	Cathode_assy	1
6	Table_assy	1

Figure S5. Final design of the seawater electrolysis system. Top left: assembly. Right: exploded view. Bottom left: subassemblies list.

The seawater electrolyzer assembly is divided into different subassemblies (part numbers 1-6). The following figures show the design detail of each subassembly of the system, the composing parts, and the material of each part (standards have not been included) which is selected to meet specifications with technical feasibility and costs.

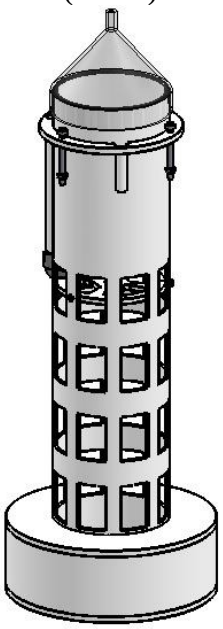
Part 1. The floatation body includes the floatation system and the O_2/Cl_2 chamber (dome).

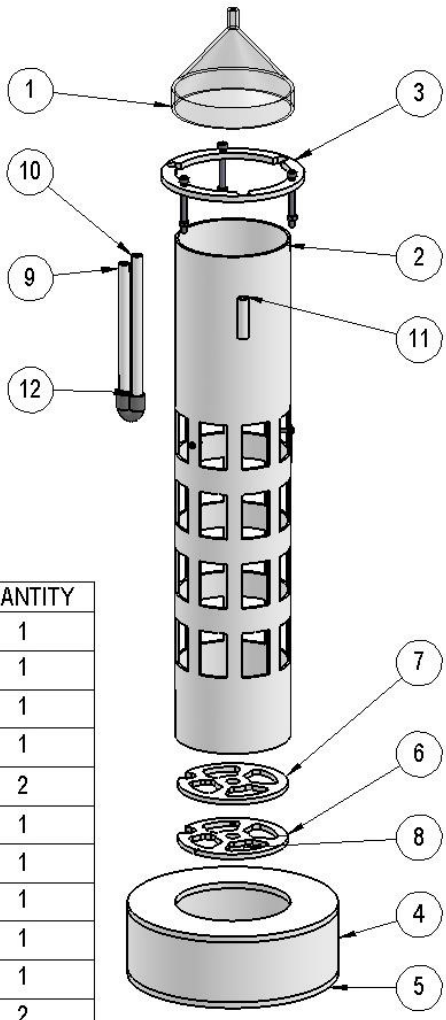


PN	PART NAME	MATERIAL	QUANTITY
1	Dome	Glass	1
2	Floatation_base	Wood	1
3	Floatation_ring	LDPS	1

Figure S6. Detail of the floatation body subassembly. Top: assembly. Middle: exploded view. Bottom: parts list.

Part 2. The main pipe includes the cathode housing and fixing system, a ballast pack for the stability and weight compensation of the whole system, the connection pipes and the H_2 recovery chamber (funnel).

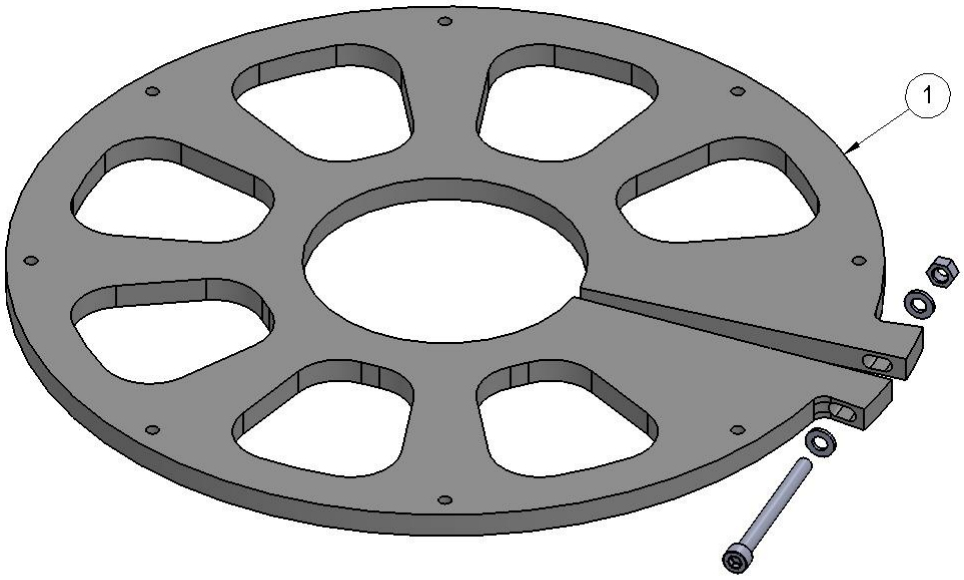




PN	PART NAME	MATERIAL	QUANTITY
1	Funnel	Glass	1
2	Central_pipe	PVC	1
3	Central_pipe_fixture	PVC	1
4	Ballast_pipe	PVC	1
5	Ballast_cover	PVC	2
6	Cathode_fixture	PVC	1
7	Cathode_fixture	PVC	1
8	Cathode_cap	PVC	1
9	Wire_pipe	PVC	1
10	Wire_pipe	PVC	1
11	Wire_pipe	PVC	2
12	Wire_U	PA	1

Figure S7. Detail of the main pipe subassembly. Top left: assembly. Right: exploded view. Bottom left: parts list.

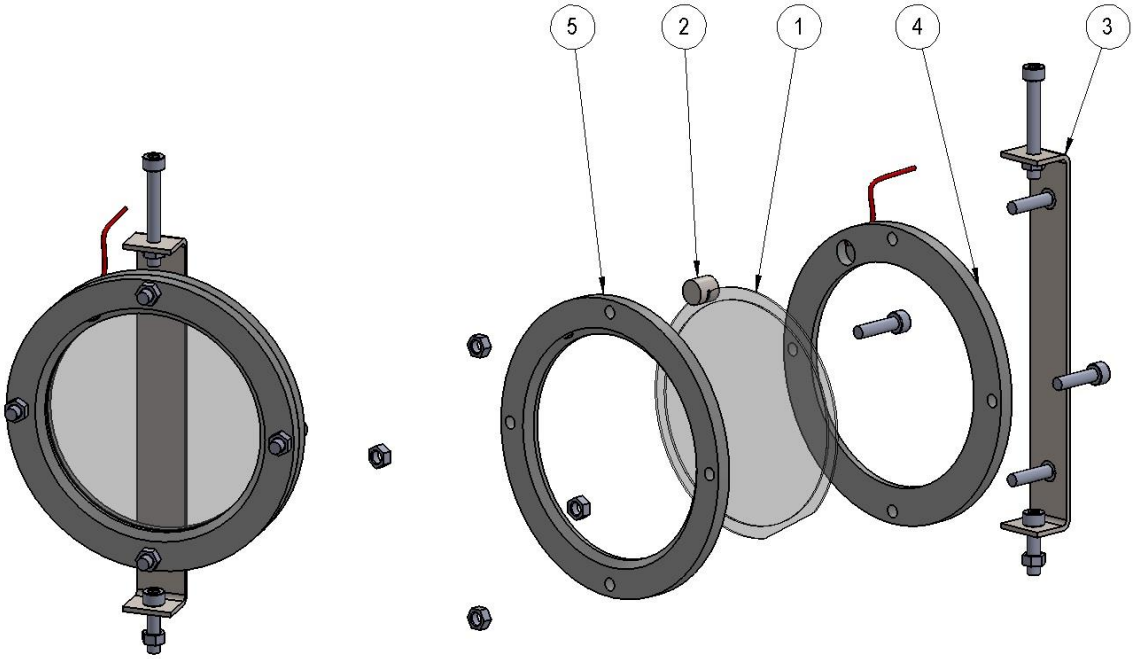
Part 3. The anodes support includes a circular base for the fixing of the anodes.



PN	PART NAME	MATERIAL	QUANTITY
1	Ring	HDPE	1

Figure S8. Detail of the anodes support subassembly. Top: exploded view. Bottom: parts list.

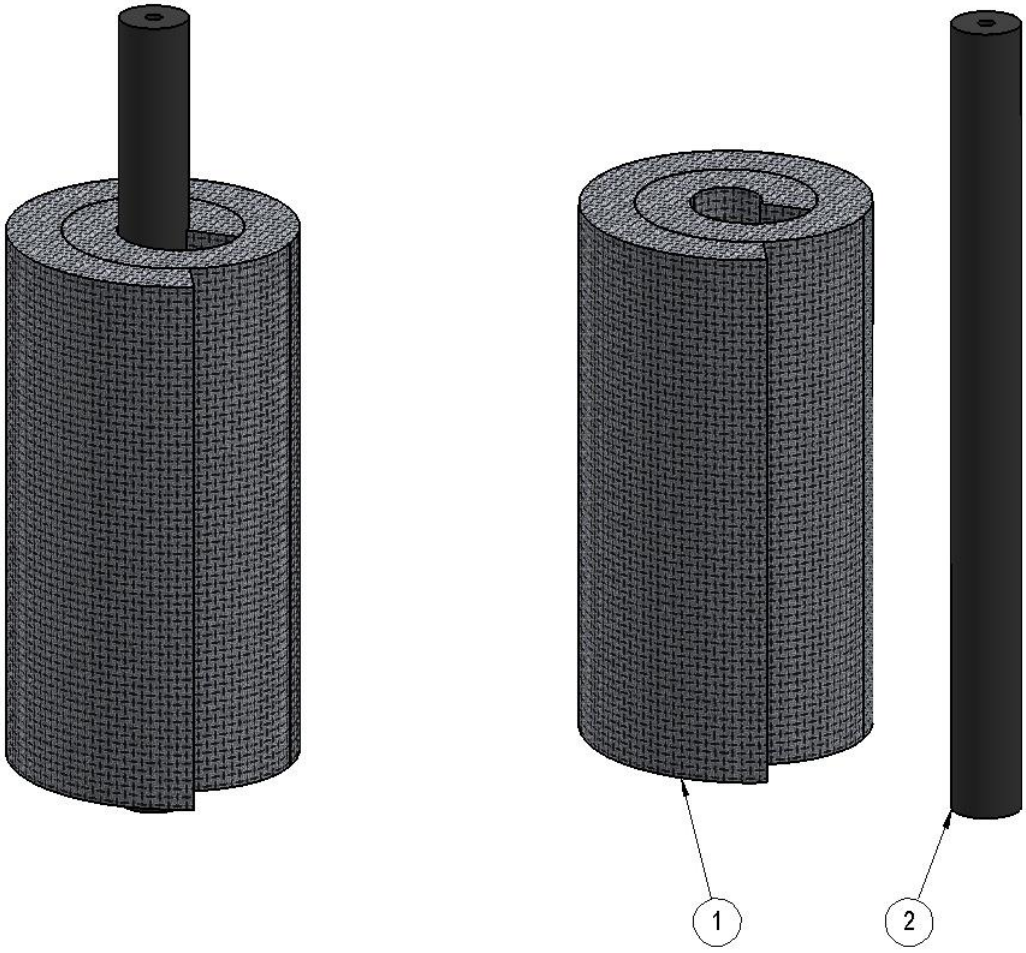
Part 4. The anode subassembly includes the anode, the supports and the connection.



PN	PART NAME	MATERIAL	QUANTITY
1	Anode	Si/SiO2/FTO	1
2	Anode_connection	Ti	1
3	Anode_support	PVC	1
4	Back_support	HDPE	1
5	Front_support	HDPE	1

Figure S9. Detail of the anodes subassembly. Left: assembly. Right: exploded view. Bottom: parts list.

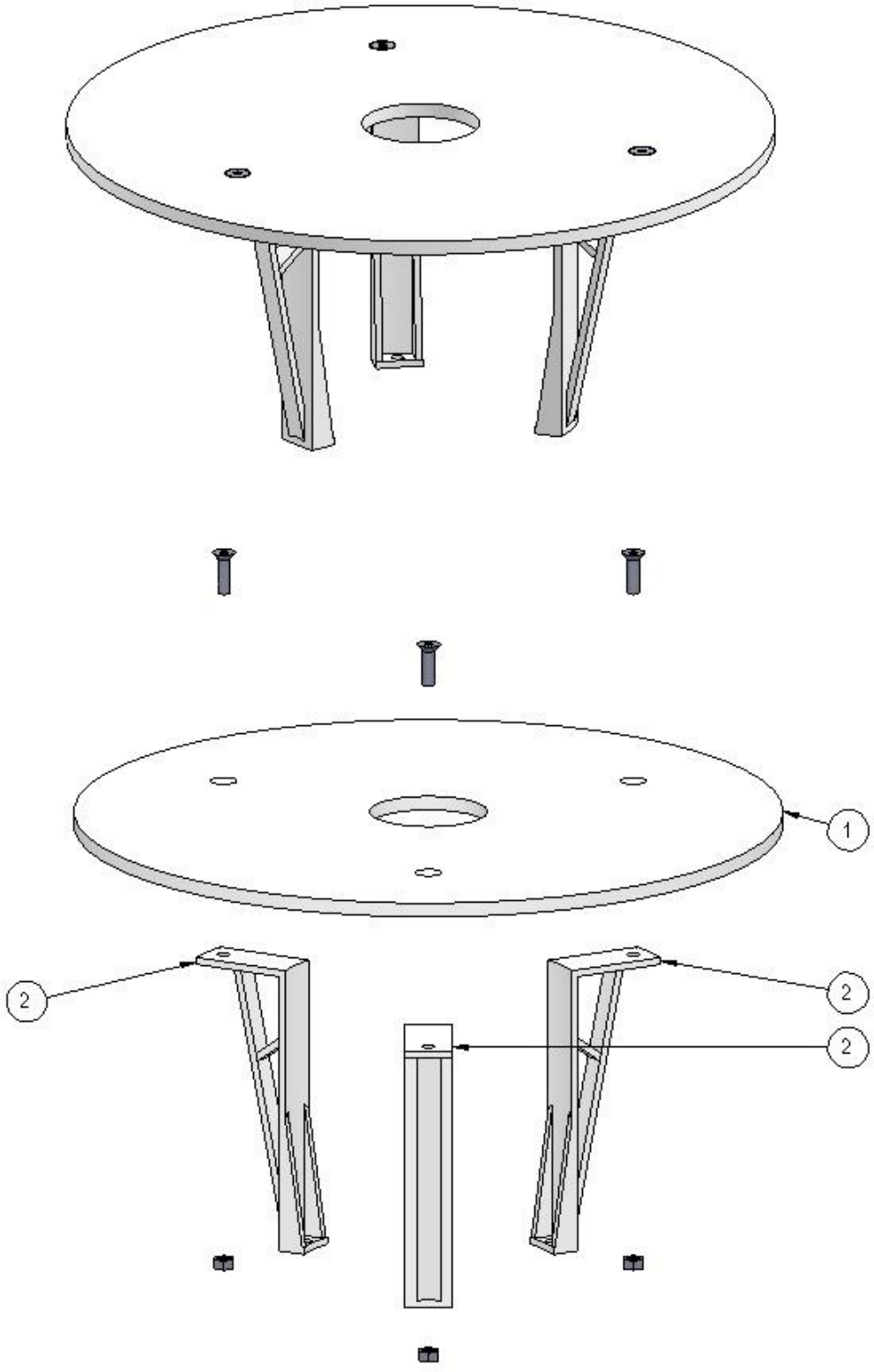
Part 5. The cathode subassembly includes the cathode (rolled carbon felt) and a support for the cathode (graphite bar).



PN	PART NAME	MATERIAL	QUANTITY
1	Cathode	Carbon Felt	1
2	Cathode_support	Graphite	1

Figure S10. Detail of the cathode subassembly. Left: assembly. Right: exploded view. Bottom: parts list.

Part 6. The table subassembly includes the table itself for the auxiliary equipment.



PN	PART NAME	MATERIAL	QUANTITY
1	Table	PVC	1
2	Table_support	ABS	3

Figure S11. Detail of the table subassembly. Top: assembly. Middle: exploded view. Bottom: parts list.

Section S4. Prototype construction

For the construction of the seawater electrolyzer system, conventional manufacturing (machining, cut, bending...) and additive manufacturing techniques (FDM, SLS) are considered, to make the prototype technically feasible and cost affordable.

Table S1. Bill of Materials.

Assembly	Part Name	Quantity	Material	Technology
1	**Floatation body**	**1**		
1.1	Floatation base	1	Wood	Machining
1.2	Floatation ring	1	HDPS	Cut
1.3	Dome	1	Glass	Gravity mould
1.4	Bolt DIN912	4	PA	Standard
1.5	Nut DIN934	4	PA	Standard
2	**Main pipe**	**1**		
2.1	Central pipe	1	PVC	Machining
2.2	Central pipe fixture	1	PVC	Machining
2.3	Bolt DIN912	3	PA	Standard
2.4	Nut DIN934	3	PA	Standard
2.5	Ballast	1		
2.5.1	Pipe	1	PVC	Cut
2.5.2	Cover	2	PVC	Cut
2.6	Cathode fixture	2	PVC	Machining
2.7	Bolt DIN912	3	PA	Standard
2.8	Cathode cap	1	PVC	Standard
2.9	Wire pipe	4	PVC	Cut
2.10	Wire U	1	PA + resin	SLS
2.11	Funnel	1	Glass	Blowing
3	**Anodes support**	**1**		
3.1	Ring	1	HDPE	Machining
3.2	Bolt DIN912	1	PA	Standard
3.3	Nut DIN934	1	PA	Standard
3.4	Washer DIN125	2	PA	Standard
4	**Anode assembly**	**8**		
4.1	Anode	1	Si	Coating
4.2	Back support	1	HDPE	Machining
4.3	Front support	1	HDPE	Machining
4.4	Anode connection Ti	1	Ti	Machining
4.5	Anode support	1	PVC	Cut + Bend
4.6	Bolt DIN912	4	PA	Standard
4.7	Bolt DIN912	1	PA	Standard
4.8	Bolt DIN912	1	PA	Standard
4.9	Nut DIN934	6	PA	Standard
5	**Cathode assembly**	**1**		
5.1	Cathode	1	Carbon felt	Standard
5.2	Cathode support	1	Graphite	Standard

Table S1. (Cont.)

Assembly	Part Name	Quantity	Material	Technology
6	**Table assembly**	**1**		
6.1	Table	1	PVC	Machining
6.2	Table support	3	ABS	FDM
6.3	Bolt DIN7991	3	PA	Standard
6.4	Nut DIN934	3	PA	Standard

Volumes and weights are used to calculate the floatability of the seawater electrolyzer system, which has to be precise in order to guarantee the electrodes are under water and water does not go into the gases recovery chambers. Calculation summary is shown below:

$$G = Gravity\ force = m_{system} \cdot g \quad \text{(S1)}$$

$$F = Floatablity = V_{submerged} \cdot \rho_{fluid} \cdot g \quad \text{(S2)}$$

Where m is mass, V is volume and g for gravity force.

$F < G$	The system does not float or The system floats below the desired floatability line
$F = G$	The system floats on the desired floatability line
$F > G$	The system floats over the desired floatability line

Considering the weights and volumes of all components of the electrolyzer system, the floatability of the prototype is calculated:

Gravity force	136,51 N
Floatability	164,51 N

Section S5. Prototype assembly

The following images show the assembly of the seawater electrolyzer system with all the components manufactured and assembled.
First, the main structure of the seawater electrolyzer system was assembled:



Figure S12. Main structure of the seawater electrolyzer system.



Figure S13. Detail of the collection chambers of the gases: dome and funnel.



Figure S14. Top view of the assembly of the seawater electrolyzer system.



Figure S15. Detail of the cathode and anodes supports and the ballast.

Then the floatability ring in order to guarantee the floatation of the system:

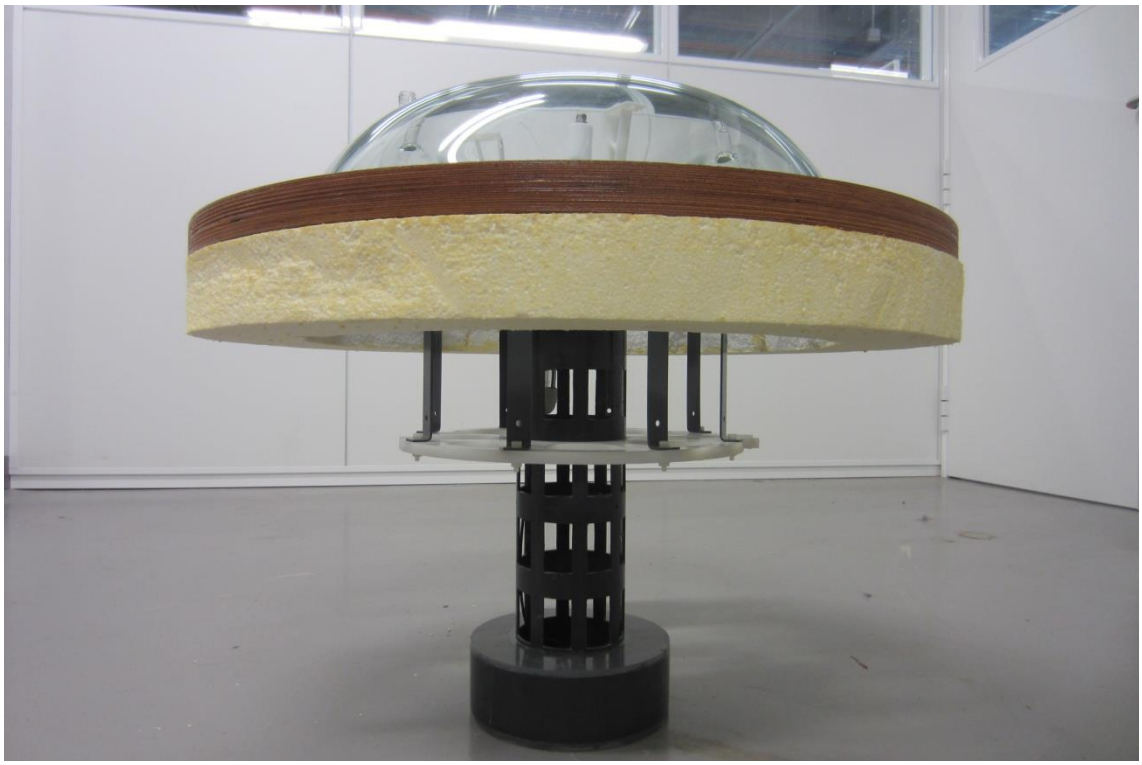


Figure S16. Floatability ring assembly on the seawater electrolyzer system.

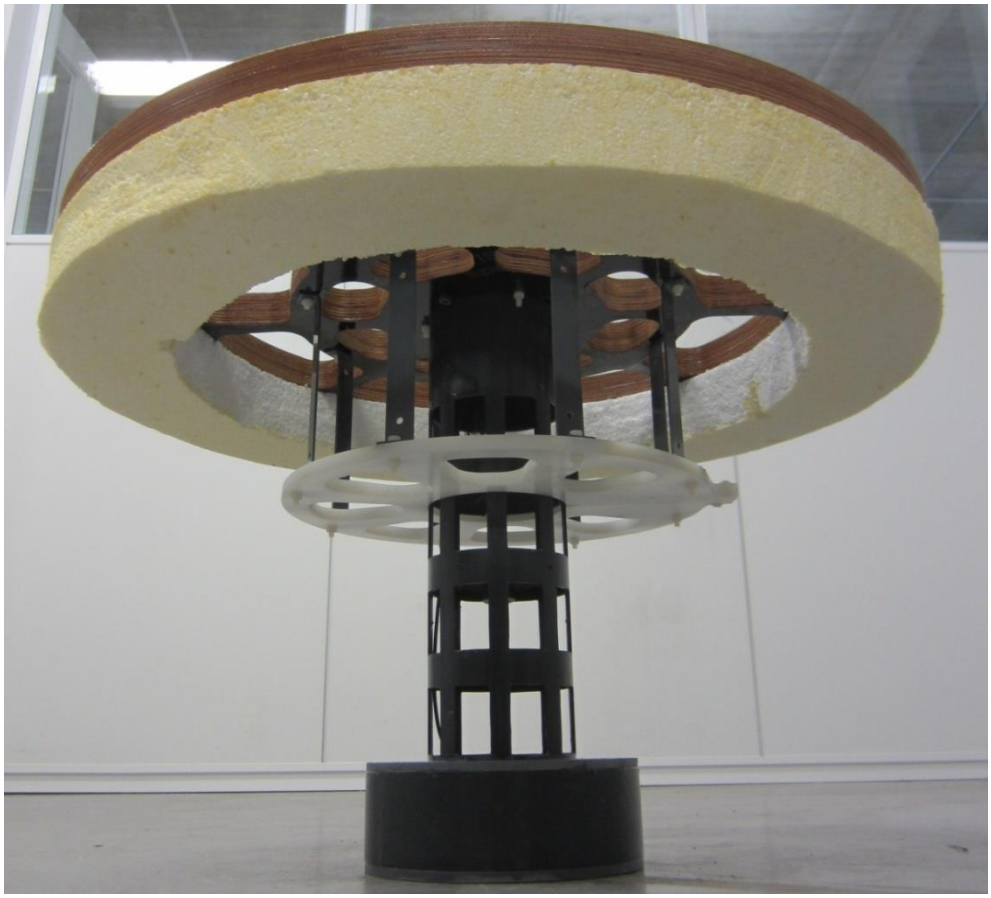


Figure S17. Detail of the floatability ring assembled on the seawater electrolyzer system.

Then, the assembly of the anodes with their supports and connections was carried out:



Figure S18. Assembly of the anodes on the seawater electrolyzer system.



Figure S19. Detail of the anodes assembled on the seawater electrolyzer system.

Finally, the support for connections and auxiliary equipment was coupled:

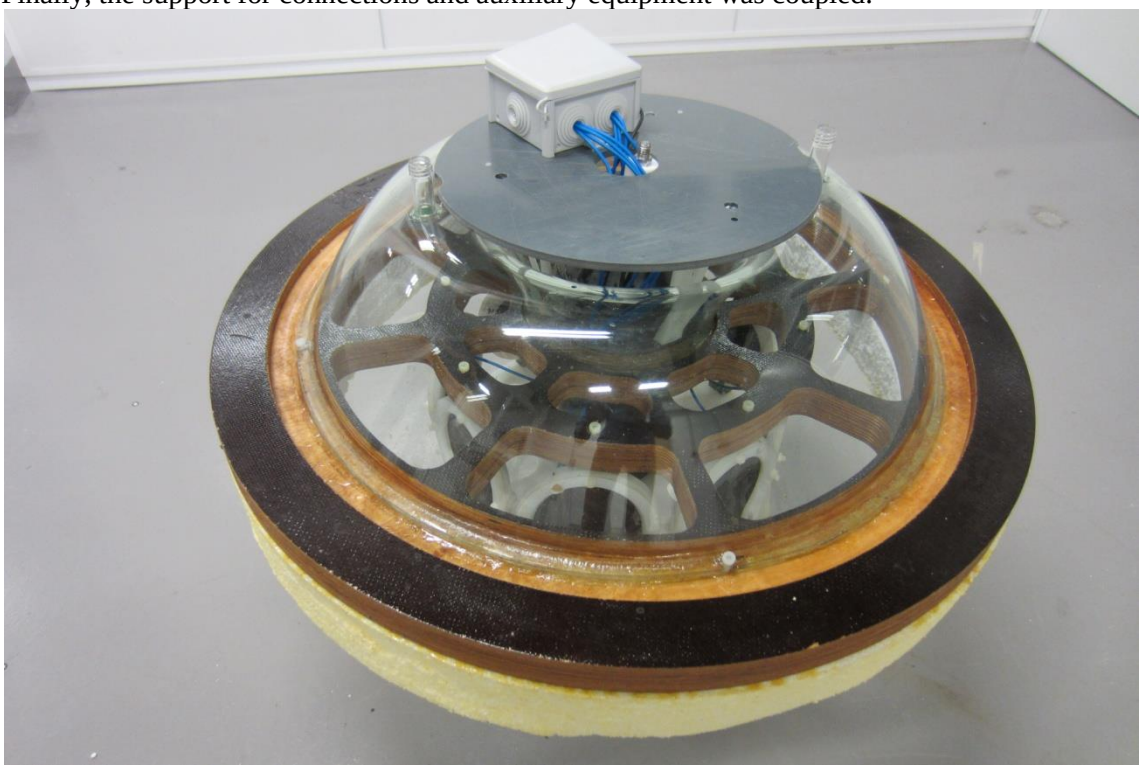


Figure S20. View of the support, connections and housing.

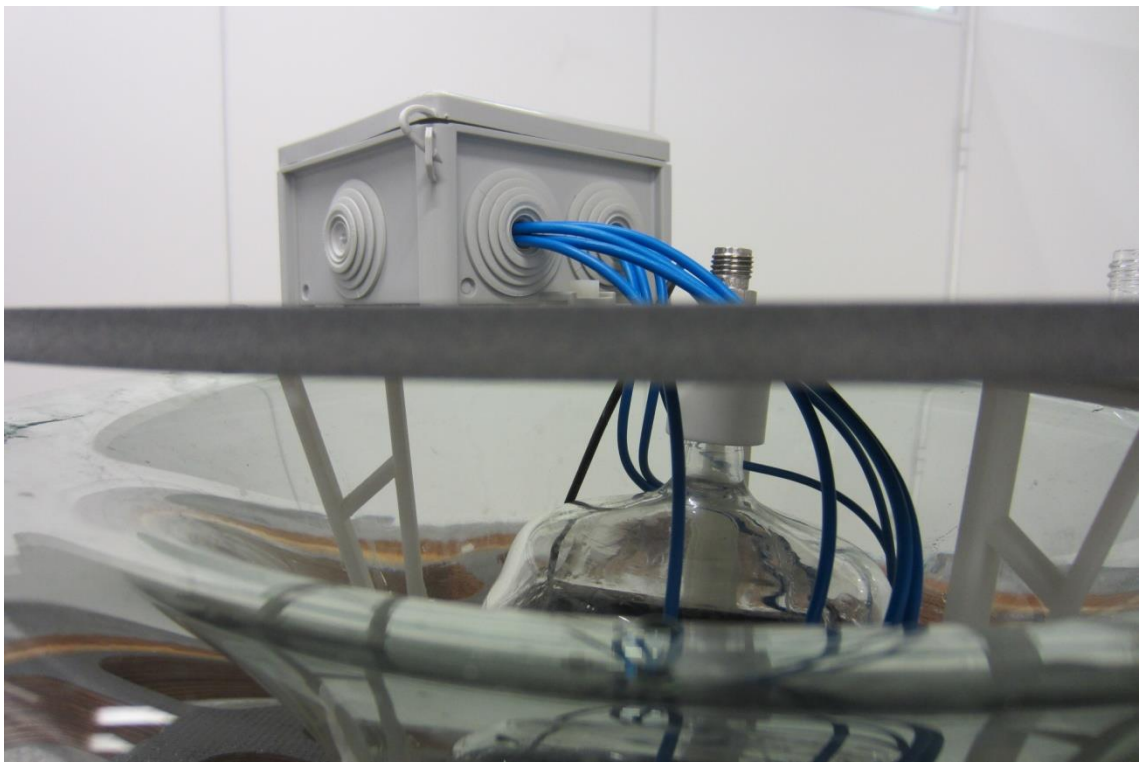


Figure S21. Detail of the connections and housing.

Section S6. Prototype evaluation

The prototype was finally tested in a 1000 L-tank containing 650 L seawater, using a high-flow pump of 5 m^3 h^{-1} for stirring.

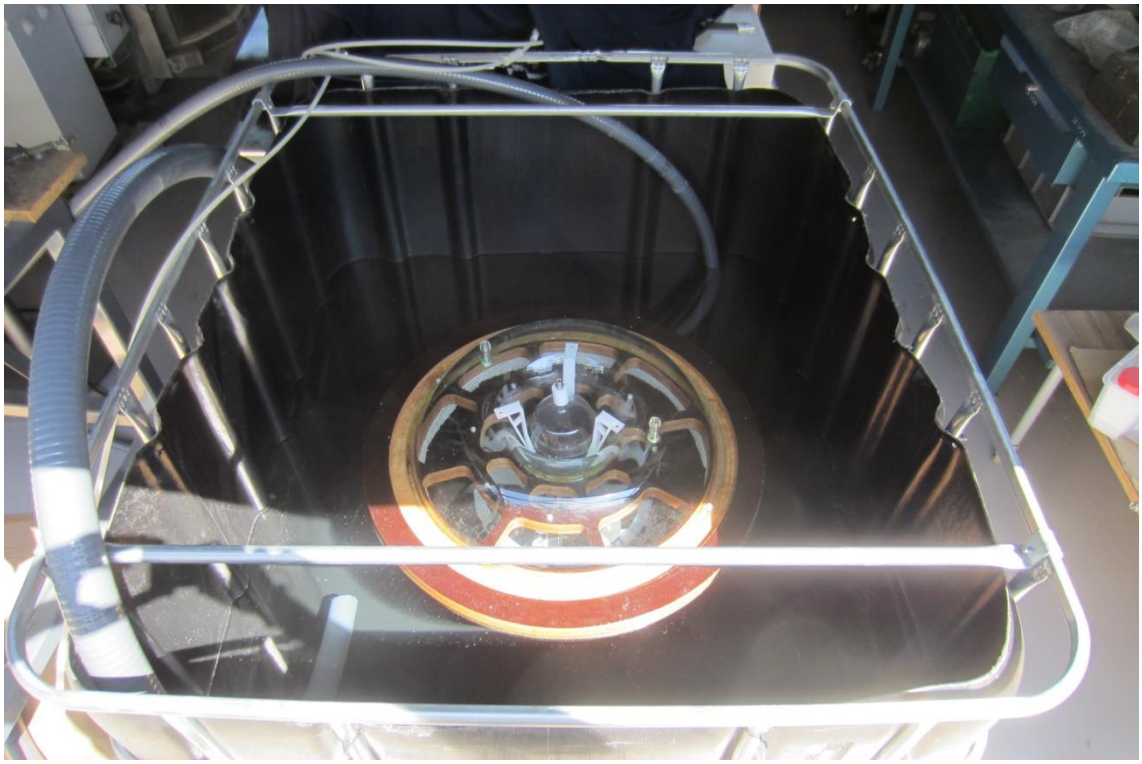


Figure S22. Seawater electrolyzer prototype on the tank used for the testing stage.

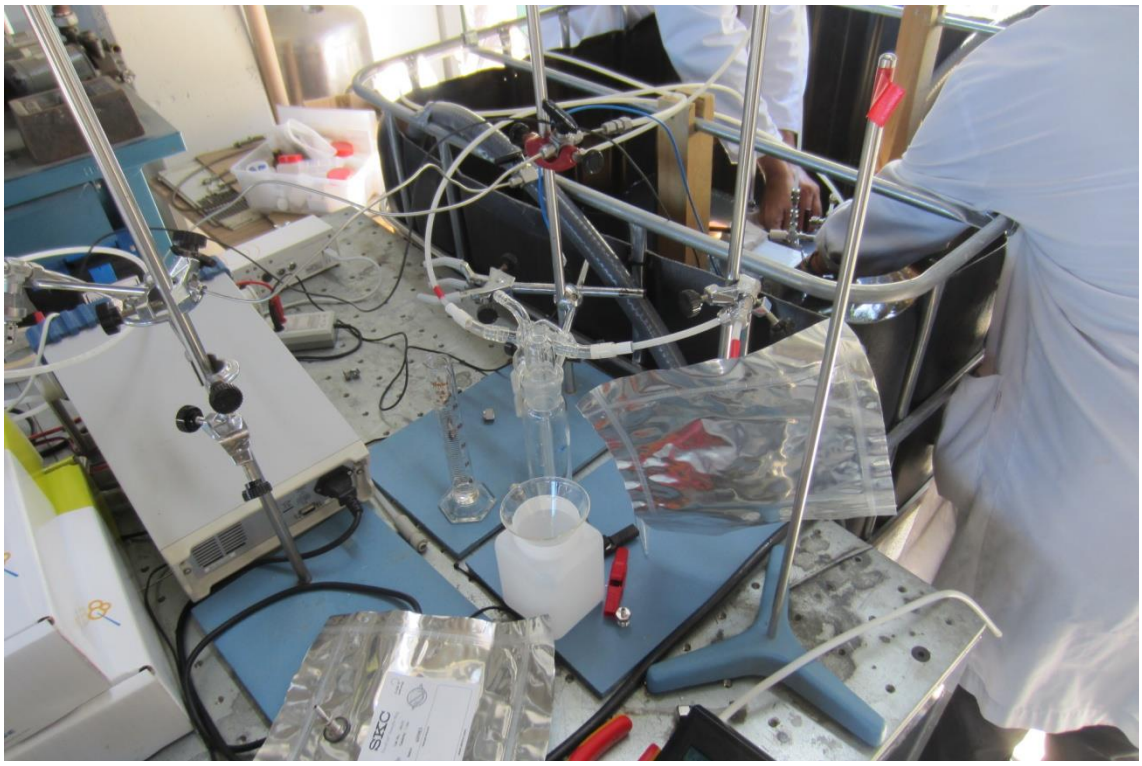


Figure S23. Hydrolyser auxiliary devices on the prototype validation scenario.

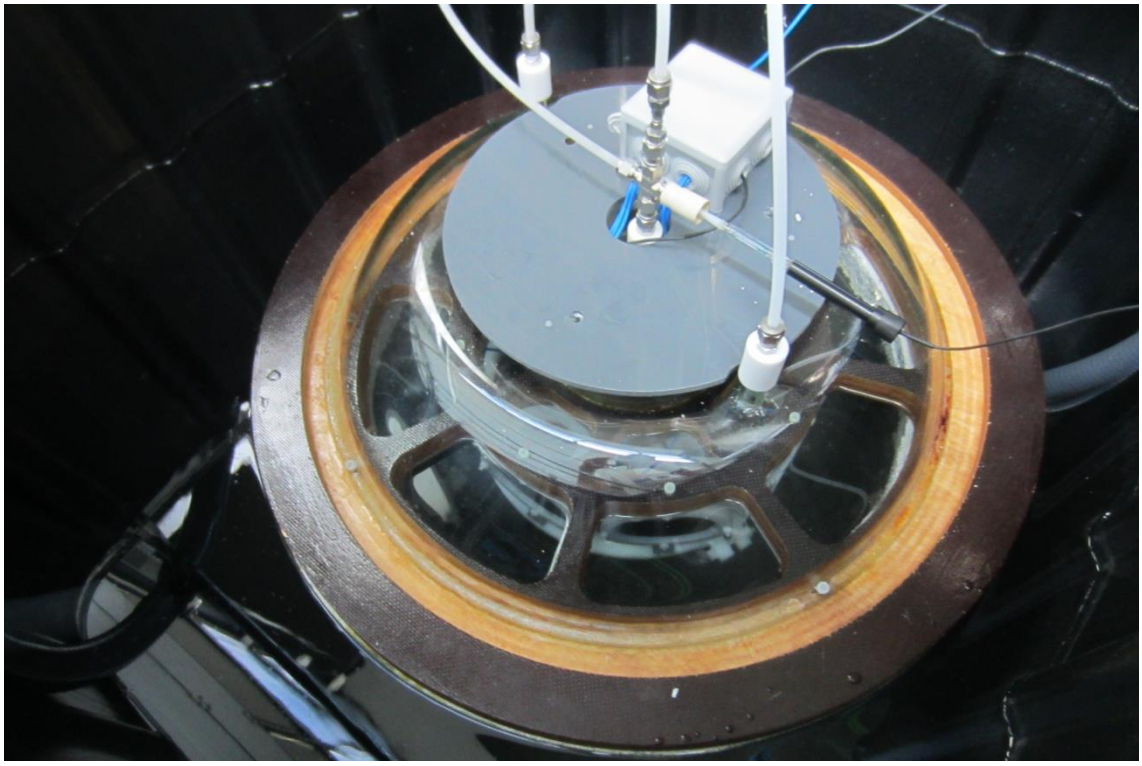


Figure S24. Connections for the gases and electric source on the seawater electrolyzer system.

Section S7. Hydrogen evolution measurement

H_2 concentration in the cathode gas headspace was in-situ monitored with a H_2 sensor (Unisense) during a chronoamperometry at 2.7 V and lasted far beyond the electrochemical test (which was stopped after 2500 s), due to the long response delay of this system. After 15000 s the sensor signal started to decay due to hydrogen purging in the funnel and, at this moment, collected gas samples were analyzed by gas chromatography (Agilent 490 microGC).

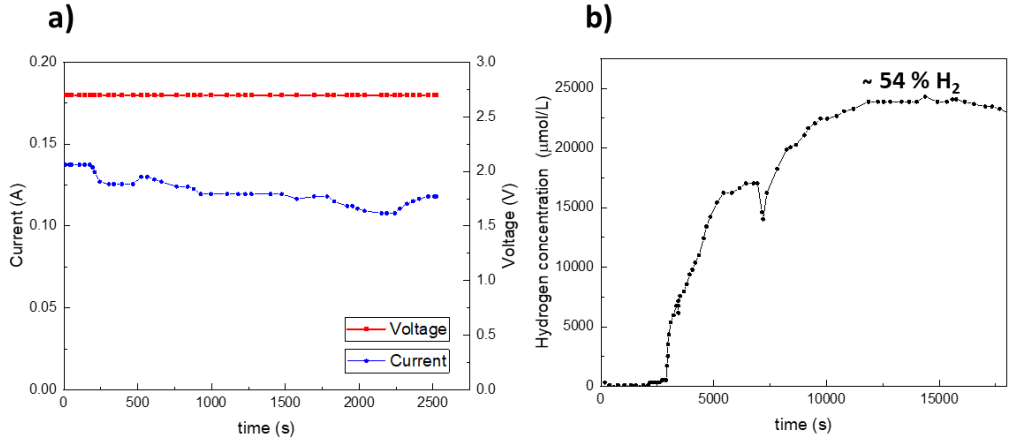


Figure S25. (a) Chronoamperometry measurement at 2.7 V with the seawater electrolyzer system, using PS/SiOx/FTO/CoFe-PB (1016 cm^2) and C-felt (150 cm^3). (b) In-situ measurement of hydrogen concentration in the cathode gas headspace with H_2 sensor.

Table S2. Gas chromatography analysis of cathode gas headspace at 15000 s of test performed in Figure S25.

Analysis Nr.	H_2 / vol.%	O_2 / vol.%	N_2 / vol.%	**H_2 / vol.% (air-free recalculated)**
1	59.63	6.05	24.36	**90.04**
2	59.88	5.98	24.28	**90.14**
3	59.83	6.01	24.38	**90.22**
Average	59.78	6.01	24.34	**90.13**

Table S3. Comparison of relative O_2 and N_2 concentration in the cathode gas headspace and in air sample.

Sample	O_2 / vol.%	N_2 / vol.%
Prototype (average)	19.81	80.19
Air	20.94	78.08

Section S8. Solid precipitate on cathode

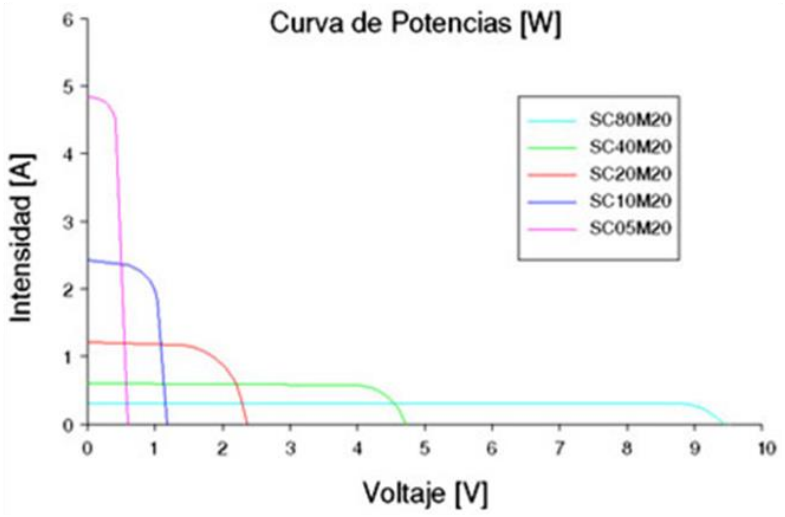
Table S4. Elemental analysis by ICP-MS on precipitate sample scratched from carbon felt and graphite rod after all chronoamperometry measurements performed in the seawater electrolyzer system.

Element	Concentration / mg kg^{-1}
Mg	326244
Na	39605
Ca	16297
S	7833
Si	2401
K	1088
Zn	378.2
B	350.6
Sr	308.3
P	116.2
Fe	71.7
Ba	34.92
Al	16.2
Mn	8.54
Ga	6.86
Ti	6.58
Sn	3.02
Li	1.59
Co	1.51
Cu	1.49
Se	1.42
As	1.11
V	1.03
Cr	0.93
Ni	0.83
Mo	0.8
Rb	0.36
Pb	0.20
Be	<0.1
Ge	<0.1
Ag	<0.1
Cd	<0.1
In	<0.1
Sb	<0.1
Cs	<0.1
W	<0.1
Pt	<0.1
Au	<0.1
Hg	<0.1
Tl	<0.1
Bi	<0.1

Section S9. Choice of photovoltaic cell

Based on the obtained electrocatalytic performance of the seawater electrolyzer, the authors propose to couple a commercial modular photovoltaic cell of ClickCell for simplicity and flexibility.

a)



b)

	Voc [V]	Isc [A]	Vmpp [V]	Impp [A]	Pmax [W]	Medidas [mm]
CS05M20	0,59	4,84	0,50	4,40	2,20	166 x 166 x 18
CS10M20	1,18	2,42	1,00	2,20	2,20	166 x 166 x 18
CS20M20	2,36	1,21	2,00	1,10	2,20	166 x 166 x 18
CS40M20	4,72	0,60	4,00	0,55	2,20	166 x 166 x 18
CS80M20	9,44	0,30	8,00	0,253	2,20	166 x 166 x 18

Figure S26. (a) Power curves and (b) technical specifications of ClickCell modules.

The specifications of the photovoltaic cell must match the energy requirements of the electrolyzer. For this purpose, we have estimated the maximum current that would be expected to be reached when operating the seawater electrolyzer containing 1016 cm^2 anode at 2.7 V cell voltage, by assuming the current density actually obtained at laboratory scale at this potential, i.e. 1.75 mA cm^{-2}_{anode} (Figure 3 in the manuscript) and not considering any inefficient scaling up issue or additional mass transport limitations. In this way, the expected energy requirements would be 1.8 A at 2.7 V, and among the Clickcells, the most convenient configuration would be four CS40M20 cells connected in parallel (Table S5).

Table S5. Power specifications of the ClickCell modules.

	1 module	4 modules in parallel
Vmpp [V]	4	4
Impp [A]	0.55	2.2

To fix the voltage at the 2.7 V needed and to avoid an overpower, a regulator (Table S6 and Figure S27) should be implemented. This small electronic device receives the power from the cells (a maximum of 4V) and returns a maximum of 2.7V (or the voltage needed).

Table S6. Technical specifications of the required power regulator.

	Minimum	Typical	Maximum
Input voltage	2.5	4	7
Output voltage	2.7	2.7	2.7
Output current	-	-	3

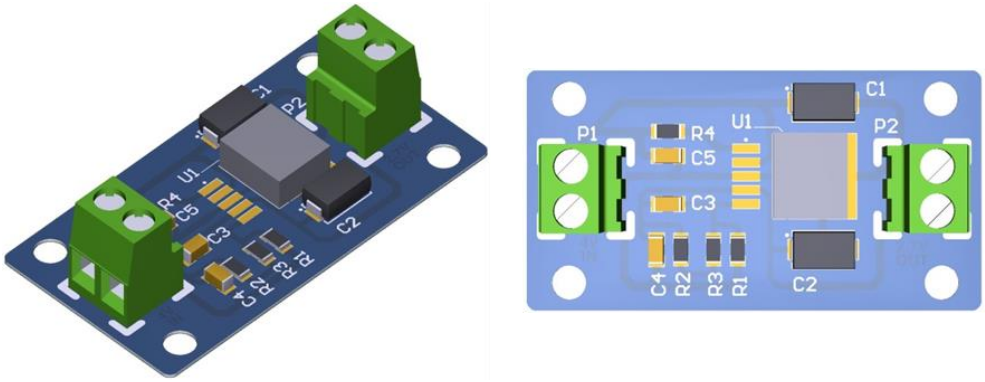


Figure S27. Design of the Printed Circuit Board (PCB) for the voltage regulator.

Then, considering the efficiency of the solar cell CS40M20 around 8.18% (equation 1), with a solar intensity of 110 mW/cm^2 and considering an effective area of 276 cm^2, the overall solar-to-hydrogen efficiency can be estimated as 7.37%, considering 90.13% of Faradaic efficiency to hydrogen (Table S2).

$$\eta = \frac{FF \times Voc \times Isc}{Pin} \quad (1)$$

Where:
V_{oc} is the open-circuit voltage;
I_{sc} is the short-circuit current;
FF is the fill factor (around 0.7);
P_{in} is the solar power;
η is the efficiency.